

## **CHAPTER II**

### **THEORETICAL BACK GROUND AND LITERATURE REVIEW**

#### **2.1 Introduction**

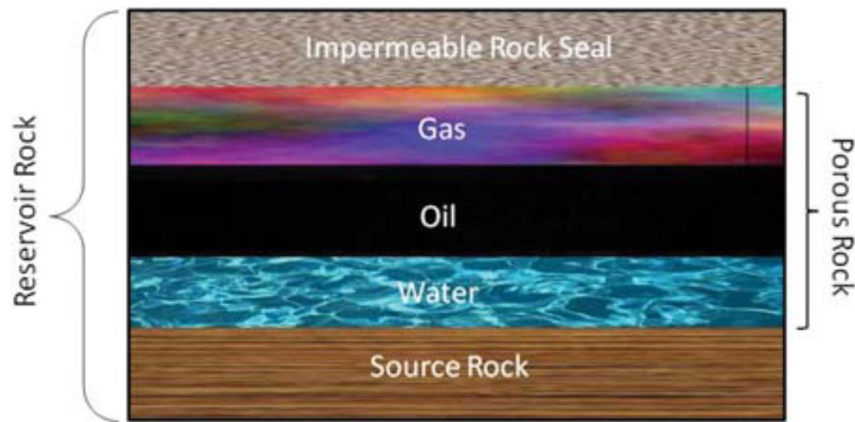
Reusing of produced water for injection, disposal and stimulation techniques, represent great challenge in oilfield operation and required prior treatment for several constituents. This chapter describes an overview of oilfield produced water, volume of produced water, composition of produced water, problem caused by produced water, the management issues and treatment techniques that possible in oil and gas industry and use for several years ago, to reduce the effect of these waters environmentally. Unfortunately, sometimes these happen without prior treatment which could be because the cost of treatment.

#### **2.2 Oilfield Produced Water**

Produced water is the largest wastewater stream in the oil exploration and production process. It is slightly acidic and sits below the hydrocarbons in porous reservoir media (see figure) (Igunnu & Chen 2012). During well drilling and completion, some water will return to the surface, known as the fracturing flowback or produced water (a water based solution that flows back to the surface during and after the completion of hydraulic fracturing). There is no established way to define flowback and produced water. Sometimes they are identified according to the time of occurrence, the rate of return or the chemical composition(Khatib & Verbeek 2003).

Produced Water is generated from conventional oil and gas production, as well as the production of unconventional sources such as coal bed methane, tight sands, and gas shale. The most widely used form of produced water disposal is re-injection into accepting formations. However, as the water cut increases, re-injection may not remain a feasible option for produced water treatment. Both flowback and produced water are comprised of fracture fluid and formation water, but they have different concentrations of chemical components.

The concentration of constituents and the volume of produced water differ dramatically depending on the type and location of the petroleum product.



**Fig 2.1 Sketch of A Typical Reservoir (Igunnu & Chen, 2012)**

### **2.3 Volumes of Produced Water**

In 1999, estimated about 77 billion barrels of produced water were generated worldwide for the whole year, which represents more than 200 million barrels per day for the entire world(Khatib & Verbeek, 2003). Produced water volume annual estimates for onshore oil and gas wells in the United States for the years 1985, 1995, and 2001(Veil & Clark, 2010).

In United States 2014, m18 billion barrel (bbl) of produced water, 149 million (bbl) of drilling waste and 21 million (bbl) of associated waste generated through exploration and production operations are discharged into the environment or managed at well site(Bankole & Blauch, 2014).

Annually, produced water volumes generated from the oil and gas industry are in the range of 15 to 20 billion barrels (1 bbl = 42 U.S. gallons), equivalent to a volume of 1.7 to 2.3 billion gallons generated daily (Bybee, 2011).

It is estimated that more than 2 million gallons of water per well is being used in fracturing operations, and most of the water then is re-injected for disposal. Over 50% of this producedbrine can be reused in subsequent well fractures, and 24% can be recovered as fresh water for beneficial use (website).

Globally, 250 million barrels of water are produced daily from both oil and gas fields and more than 40% of this is discharged into the environment (Arthur et al., 2005). Reinjection is not always feasible because of geographic and cost considerations (Sullivan, et al, 2004).

To maintain the hydraulic pressure in the petroleum reservoir, which is reduced as soon as production is started, seawater is commonly pumped into the reservoir water layer below the hydrocarbons. This pressure maintenance due to water injection causes high extensions in recoverable hydrocarbons but simultaneously contributes to increased water production. In this project reused of produced water as alternative to seawater is desirable this is it solve two issues first the area of case study so from the Heglig area and to reduce the impact of huge production of water.

## **2.4 Composition Of Produced Water**

The compositions of produced water can be classified according to their constituents into organic and inorganic compounds, including dissolved and dispersed oils & grease, heavy metals, radionuclides, formation solids, salts, dissolved gases, scale products, waxes, microorganisms and dissolved oxygen (Riksheim & Johnsen, 1994). Produced water it may encompass water from reservoir (formation water), water injected into formation and any chemicals added during the production and treatment processes. Wherefore, the physical and chemical properties of produced water vary considerably depending on the geographic location of the field, the geological formation from which it comes, and the type of hydrocarbon product being produced. Several studies have been presented on the chemical and physical characteristics of produced water; Arthur and et al described major constituents of concern in produced water are (Arthur et al., 2005):

1. Dispersed oil: Oil is an important contaminant in produced water since it can create potentially toxic effects near the discharge point.
2. Dissolved Organic Compounds: They include organic acids, polycyclic aromatic hydrocarbons (PAHs), phenols and volatiles. Volatile hydrocarbons can occur naturally in produced water. Concentrations of these compounds are usually higher in produced water from gas-condensate-producing platforms than in produced water from oil producing platforms.

3. Treatment Chemicals: They include biocides, reverse emulsion breakers, and corrosion inhibitors. Corrosion inhibitors can form stable emulsions. Some chemicals are highly toxic even at low concentrations such as 0.1 ppm.
4. Produced Solids: They consist of precipitated solids (scales), sand and silt, carbonates, clays, corrosion products and other suspended solids produced from the formation and from well bore operations.
5. Bacteria: Anaerobic bacteria present in produced water may lead to corrosion.
6. Metals: Zinc, Lead, Manganese, Iron and Barium are the metals usually present in produced water. They are in general less toxic when compared to organic constituents. But they may precipitate to form undesired solids which hinder the treatment processes.
7. Salt content: Salt content can be expressed as salinity, total dissolved solids, or electrical conductivity. The salt content in produced water varies widely, from nearly freshwater to salt levels up to ten times higher than seawater.
8. Oil and grease: Oil and grease is not an individual chemical. Rather, the term "oil and grease" refers to a common test method that measures many types of organic chemicals that collectively lend an "oily" property to the water.
9. Naturally occurring radioactive material (NORM): Some of the formations holding oil and gas have small concentrations of natural radioactivity. Low levels of the radioactivity can be transferred into produced water. Generally, the radiation levels in produced water are very low and pose no risk. However, scale from pipes and sludge from tanks holding produced water can concentrate NORM.

**Table 2.1 Composition of Oilfield Produced Water(Igunnu & Chen, 2012)**

<b>Parameter</b>	<b>Minimum Value</b>	<b>Maximum Value</b>
Density (kg/m <sup>3</sup> )	1014	1140
Conductivity (mS/cm)	4200	58 600
Surface tension (dyn/cm)	43	78
pH	4.3	10
TOC (mg/l)	0	1500
TSS (mg/l)	1.2	1000
Total oil (IR; mg/l)	2	565
Volatile (BTX; mg/l)	0.39	35
Base/ neutrals (mg/l)	—	<140
Chloride (mg/l)	80	200 000
Bicarbonate (mg/l)	77	3990
Sulphate (mg/l)	<2	1650
Ammoniacal nitrogen (mg/l)	10	300
Sulphite (mg/l)	—	10
Total polar (mg/L)	9.7	600
Higher acids (mg/l)	<1	63
Phenol (mg/l)	0.009	23
Volatile fatty acids (mg/l)	2	4900

**Table 2.2 Continue- Composition of Oilfield Produced Water**

<b>Heavy metal</b>	<b>Minimum value (mg/l)</b>	<b>Maximum value (mg/l)</b>
Calcium	13	25 800
Sodium	132	97 000
Potassium	24	4300
Magnesium	8	6000
Iron	<0.1	100
Aluminum	310	410
Boron	5	95
Barium	1.3	650
Cadmium	<0.005	0.2
Copper	<0.02	1.5
Chromium	0.02	1.1
Lithium	3	50
Manganese	<0.004	175

## **2.5 Problem Cause By Produced Water**

Re- using of produced water for injection process prior to treatment causes number of problems; these problems are:

1. Excess soluble salts which can cause plants to dehydrate and die.
2. Reduced oxygen level enough to damage aquatic species.
3. Injection formation plugging due to suspended solids, which results in injection pressure increase and decrease in the produced water injection flow rate.
4. Scale problem which causes well bore clogging and fluid flow prevention(Bybee, 2005)(Georgie et al., 2001).

## **2.6 Management Issues**

This part of this chapter describes some of the many possible option or technologies that can be used to produced water in order to management. The management of produced water presents many challenges and can pose significant costs to operators. Current techniques for produced water management include several methods such as underground injection either for disposal or increasing recovery, direct discharge, reuse in oil and gas operation, and beneficial use, etc.

### **2.6.1 Injection For Disposal**

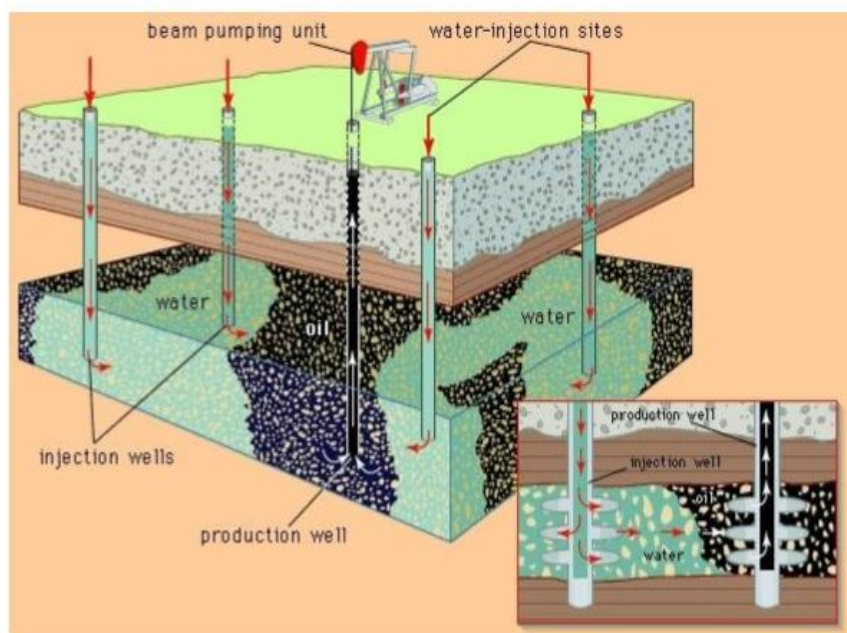
An old option for produced water management is injection for disposal and it is very important, with the increasing amount of produced water, handling of produced water has become one of the main issues in petroleum industry. Required facilities and equipment for treatment of the produced water are expensive. So disposal via injection represent a new technologies that proposed by the companies are to minimize the production of water and consequently reduce the costs of water treatment methods and look for ways that with existing facilities can handle larger volumes of water. Produced water from onshore wells is recycled and reused. There are different ways of disposing produced water, some of the common methods are:

- a. Evaporation pits
- b. Surface discharge/overboard disposal
- c. Deep aquifer injection
- d. Agricultural use (Irrigation of fruit trees or forage land...)

- e. Industrial use (Dust control, Vehicle wash water, power generation...)
- f. Desert flooding / livestock water pits
- g. Shallow water aquifer recharge (Farajzadeh, 2004).

The choice of produced water disposal methods is dependent on several factors, such as site location, regulatory acceptance, technical feasibility, cost and availability of infrastructure and equipment. In addition to these factors, poor injection or disposal water quality can compromise the effective injectivity of even high quality sandstone or carbonate formations, resulting in economic failures and the need for costly workovers and recompletions on a regular basis to facilitate injection operations.

Underground injection is the predominant practice because it requires little or no treatment and is often the least costly option. According to federal estimates, more than 90 percent of produced water is managed by injecting it into wells that are designated to receive produced water, (Information on the quality and quantity and management, 2012).



**Fig 2.2 Image of Water Injection (Brown,E. 2009)**

## **2.6.2 Direct Discharge**

According to Argonne National Laboratory's report, less than 1 percent of produced water generated from onshore oil and gas operations in 2007 was managed by discharging it to surface water. Surface discharges of produced water directly from oil and gas production sites are prohibited in much of the United States, but produced water may be discharged from an off-site treatment facility.

A report published on 2011 summarizes some efforts developed a comprehensive produced water management to eliminate or to reduce produced water direct discharges to the sea per the 2010 Offshore Waste Treatment Guidelines (OWTG), before this technologist the company was dumping a huge amount of water into the gulf of Mexico until they stopped by the Environmental Protection Agency EPA, their strategy consist of disposing the water into reservoir for maintain the pressure in the production formation, (Hebron-Project, 2011).

## **2.6.3 Reuse In Oil and Gas Operations**

Reuse of produced water on oil and gas operation includes multiple applications, such as well drilling, hydraulic fracturing, secondary oil recovery, and sustaining aquifer pressure, which require large water volumes. Use of fresh water supplies in these practices may be minimized by treating and recycling produced water resources.

### **2.6.3.1 Well Stimulation**

There are two types of main areas of interest for a stimulation treatment: Wellbore zone and its proximity and rest of a reservoir. Different types of Stimulation technique are generally used depending on the area of interest:

- Acid washing
- Matrix acidizing
- Acid fracturing
- Hydraulic fracturing



**Acid washing** is a type of stimulation to remove acid soluble scales present in the wellbore or to open perforations. Acid washing is the least expensive of all the near wellbore treatment techniques. A small quantity of acid delivered to the desired position in the wellbore reacts with scale deposits or the formation. Acid may be circulated back and forth across the perforations or formation face(Guoet, al. 2007).

**Matrix acidizing** is a type of stimulation to remove near-wellbore damage by injecting acid into the formation. The objective of matrix acidizing is to recover the original reservoir permeability or even create additional permeability (e.g. in carbonate formation). In sandstone formations, the acid attacks the clogging particles. Normally, sandstone formations are treated with hydrochloric/hydrofluoric (HCl/HF) mixtures. In carbonate formations (limestone and dolomite), the acid mainly attacks the matrix itself which creates secondary permeability. Hydrochloric acid is usually used in stimulation treatment of carbonate formations(Esmaeili & Dehghani, 2010).

**Hydraulic fracturing** is stimulation treatment by creating fractures to connect the wellbore with the undamaged reservoir. Hydraulic fracturing is usually carried out in formations with low permeability whereas matrix acidizing is performed in medium to high permeability formations ( $k > 10$  mD). Matrix acidizing treatment is regarded as inexpensive operation as compared to hydraulic fracturing in vertical wells but this is not true for horizontal wells (Guo et, al. 2008).

In this chapter, the discussion is limited and focused on hydraulic fracturing

## **2.7 Hydraulic Fracturing**

Hydraulic fracturing is a well-stimulation technique that is most suitable to wells in low and moderate permeability reservoirs. Hydraulic fracturing is required to enhance permeability and allow for commercial production of the hydrocarbon resource. Hydraulic fracturing is the creation or extension of natural fractures in the formation material.

The history of hydraulic fracturing date to 1947, by the first hydraulic fracturing treatment was completed in the Hugoton Field (Kansas) and fracking has also become a standard

treatment to improve production. Since that time, hydraulic fracturing has increased recoverable reserves more than any other technique(Gandossi, 2013).

Hydraulic fracturing has played an important role in the development American's oil and gas for resources nearly 60 years. In U.S., estimate 35,000 wells are hydraulically fractured annually and it is estimate that over one million wells have been hydraulic fractured since the first in the late1940s (American Petroleum Institute ,2010). Hydraulic fracturing technology has been used since that time for conventional and unconventional formation to stimulate the production of hydrocarbons from unconventional oil and gas reservoirs, which include shales, coalbeds, and tight sands. "Unconventional reservoirs" refers to oil and gas reservoirs whose porosity, permeability, or other characteristics differ from those of conventional sandstone and carbonate reservoirs.

There are many different applications for hydraulic fracturing, such as:(Mathis & Saucier, 1997)

- Increase the flow rate of oil and/or gas from low permeability reservoirs.
- Increase the flow rate of oil and/or gas from wells that have been damaged.
- Connect the natural fractures and/or cleats in a formation to the wellbore.
- Decrease the pressure drop around the well to minimize sand production.
- Increase the area of drainage or the amount of formation in contact with the wellbore.
- Connect the full vertical extent of a reservoir to a slanted or horizontal well.

## **2.8 Hydraulic Fracturing Fluids**

The function of Fracturing fluids are formulated to provide sufficient viscosity to transport and place the proppant in to the fracture, and should degrade or "break" into a low viscosity fluid to allow for rapid flow- back and clean up. Breaking of excessive viscosity fluid could be facilitated using mixed additive to fracturing fluids prior to inject to well or by injected breaker fluids into the well after fracturing process completed.

The fracturing fluid is a critical component of the hydraulic fracturing treatment. Its main functions are to open the fracture and to transport proppants along the length of the fracture. Consequently, the viscous properties of the fluid are usually considered the most important. However, successful hydraulic fracturing treatments require that the fluids have other special properties. In addition to exhibiting the proper viscosity in the fracture, they should break and

clean up rapidly once the treatment is over, provide good fluid-loss control, exhibit low friction pressure during pumping and be as economical as is practical (Economides and Nolte, 2000).

More than 90% of fracturing fluids are water-based according to Fink (2003). The obvious reason is that aqueous fluids are cheaper and can provide control of a broad range of physical properties as a result of additives developed over the years. Thousands of gallons of oil-based or Water-based fluids, usually made viscous by addition of a soluble polymer, are injected into a formation at an injection rate such that the pressure of the fluid at the formation is higher than the earth stress in the formation.

## **2.9 Properties of Fracturing Fluids**

The fracturing fluid must have certain physical and chemical properties to achieve successful stimulation.

- It should be compatible with the formation material.
- It should be compatible with the formation fluids.
- It should be capable of suspending proppants and transporting them deep into the fracture but should not carry it back during flow back.
- It should be an efficient fluid (i.e., have low fluid loss).
- It should be easy to remove from the formation.
- Preparation of the fluid should be simple and easy to perform in the field.
- It should be stable so that it will remain its viscosity throughout the treatment (Gandossi, 2013).

## **2.10 Types of Hydraulic Fracturing Fluids**

Many different types of fluids have been developed to provide the properties described above because reservoirs to be stimulated vary in temperature, permeability, rock composition, and pore pressure (Economides and Nolte, 2000).

The compositions of fracturing fluids mainly have been started with gelled and foamed, acids, any combination of these, and brine (salt water). By the end of 1952, many fracturing treatments were performed with refined and crude oils. These fluids were inexpensive,

permitting greater volumes at lower cost. In 1953 water started to be used as a fracturing fluid, and a number of gelling agents was developed. Surfactants were added to minimize emulsions with the formation fluid (Gandossi, 2013).

**Table 2.3 Various Types of Fluids and Techniques Used In Hydraulic Fracturing (Fink, 2003)**

<b>Type</b>	<b>Remarks</b>
Water-based fluids	Predominant
Oil-based fluids	Water sensitive; increased hazard
Alcohol-based fluids	Rare
Emulsion fluids	High pressure, low temperature
Noncomplex gelled water fracture	Simple technology
Nitrogen –foam fracture	Rapid
Complexed gelled water fracture	Often the best solution
Premixed gel concentrates	Improve process logistics
In situ precipitation technique	Reduce the concentration of the scale-forming ingredients

### **2.10.1 Water- Based Fluids**

Water-based fracturing fluids are the most common types and are widely used: Water – based fracturing fluids have many advantages compared to oil-based fluids.

1. Water-based fluids are economical. The base fluid, water, is much cheaper than oil, condensate, methanol, or acid.
2. Water-based fluids yield increased hydrostatic head compared with oil, gases, or methanol.
3. Water-based fluids are incombustible; hence they are not a fire hazard.
4. Water-based fluids are readily available.
5. Water-based fluids are easily viscosified and controlled.

- **Linear Fracturing Fluids**

Linear fracturing fluids are fracturing fluids without chemical crosslinked structures. The need to thicken water to help transport proppant, to decrease fluidloss, and to increase fracture width was apparent to early investigators.

**Table 2.4 Different Fluids Used for Hydraulic Fracturing and Their Compositions (EPA, 2004)**

<b>Based fluids</b>	<b>Fluid type</b>	<b>Main composition</b>
Water based	Silica water	Water + sand (chemical +additives)
	Linear fluid	Gelled water, GUAR<HPG,HEC,CMHEC
	Cross-linked	Cross liker+ HPG, CMHPG, CMHEC
	Viscoelastic Surfactant gel fluid	Electrolite + surfactant
Foam based	Water based foam	Water and foamer + N <sub>2</sub> or CO <sub>2</sub>
	Acid based foam	Acid and foamer + N <sub>2</sub>
	Alcohol based foam	Methanol and foamer N <sub>2</sub>
Oil based	Linear fluids	Oil , gelled oil
	Cross-link fluid	Phosphate Ester gels
	Water Emulsion	Water + oil + Emulsifiers
Acid based	Linear	-
	Cross-link	-
	Oil emulsion	-
Alcohol based	Methanol /water mixes or 100% methanol	Methanol + water
Emulsion based	Water –oil- emulsions	Water + oil
	CO <sub>2</sub> + Methanol	CO <sub>2</sub> +water+methanol
Other fluids	Liquid co <sub>2</sub>	CO <sub>2</sub>
	Liquid nitrogen	N <sub>2</sub>
	Liquid helium	He
	Liquid natural gas	LPG

Starch had been used as the first water viscosifiers to thicken and to decrease the fluid loss in drilling mud (Economides (2007)). Other linear gels used today as fracturing fluids are hydroxypropyl guar (HPG), hydroxyethylcellulose (HEC), carboxymethyl HPG (CMHPG), xanthan gum, and in some rare case, polyacrylamides. HPG was developed primarily to reduce the residue obtained from guar gum and to achieve greater temperature stability (Department of Energy, 2004).

Young et, al. (1998) showed that the hydrophobically modified hydroxybutyl guar (HMHBG) has improved properties over native guar, HPG, and hydroxybutyl guar (HBG). It exhibits high viscosities at low shear rates and higher extensional viscosities. In order to achieve deep penetration of proppant or of acid away from the wellbore, the higher viscosity crosslinked fracturing fluids are the better option.

- **Crosslinked Fracturing Fluids**

Crosslinked fracturing fluids were advanced processes in hydraulic fracturing technology. With linear gels, the only means to obtain increased viscosity is to increase the polymer concentration (Guo, 2007). Crosslinked fluids eliminated many of the problems when fracture-treating deep hot reservoir using linear gels. The earliest cross linkers were borates and antimony metal cross linkers. The metals are dispersed between the polymer strands and an attraction occurs between the metals and the hydroxyl or carboxy groups. This interaction takes a gel system from a true fluid to a pseudoplastic fluid. The borate fracturing fluid was a high pH-system, typically in the pH 10 range, while the antimony was approximately pH 3 to 5 (Fluids, 2004). Different crosslinked had been used such as aluminium, chromium, copper, manganese, titanium chelates, and zirconium chelates.

The main advantages of using a crosslinked fluid than a linear fluid are:

1. Much higher viscosity can be achieved in the fracture with a comparable gel loading.
2. The system is more efficient in fluid loss control.
3. A crosslinked fluid has better proppant-transport capabilities.
4. A crosslinked fluid has better temperature stability.
5. A crosslinked fluid is more cost-effective per pound of polymer.

### **2.10.2 Oil-Based Fracturing Fluids**

The only advantage of using oil-based fracturing fluids in certain situations is to avoid formation damage to water-sensitive oil-producing formations that might swell if water is introduced. The first disadvantage of using oil-based fracturing fluids is the fire hazard. Another disadvantage is the higher pumping friction of an oil-based fluid than a delayed, crosslinked water-based fluid system. Pumping pressures are also higher due to lack of

hydrostatic head of the hydrocarbon compared with water. Additionally, the temperature stability of a delayed, crosslinked water-based system is more predictable in high-temperature well. The preparation and quality control of gelling crude oil require much more care than those of water-based fluids(Fluids, 2004).

### **2.10.3 Alcohol-Based Fracturing Fluids**

In fracturing fluids, alcohol has found wide use as a temperature stabilizer because it acts as a hydrogen scavenger and has frequently been used for the removal of water blocks because alcohol reduces the surface tension of water. Methanol based fracturing fluids, particularly at higher concentrations, present difficulty in the controlled degradation of the base fluid. Very high concentrations of any type of breaker are required for complete degradation. The primary benefits of methanol relate to low surface tension, miscibility with water, removal of water blocks, and compatibility with water-sensitive formations (Fluids, 2004).

### **2.10.4 Emulsion-Based Fracturing Fluids**

The two basic types of oil/water emulsions are oil external and water external. An oil-external emulsion is a two-phase system where oil is the continuous phase and water is emulsified in the oil. A water-external emulsion has water as continuous phase and oil as the discontinuous phase. Water-external emulsions have lower friction pressures because of the low viscosity of water compared with oil. There is a tendency to achieve friction reduction with the polymers in the water phase of water-external emulsion. The pumping pressures of the water-external emulsions are somewhat higher than for typical conventional crosslinked fracturing fluid but much lower than the oil-external emulsions(Fluids, 2004).

### **2.10.5 Foam-Based Fracturing Fluids**

Foam fracturing fluids are simply a gas-in-liquid emulsion. The gas bubbles provide high viscosity and excellent proppant-transport capabilities. There are several advantages of foam based fracturing fluids. The most obvious are minimizing the amount of fluid placed in the formation and improving recovery of fracturing fluid by the inherent energy in the gas. The inherent energizing capabilities of the fluid caused by entrained gas assist in rapid

cleanup or simply promote cleanup in low-pressure formations. However, foam based fracturing fluids have several disadvantages. Much more care must be taken in running a foam fracturing treatment from a mechanical point of view. Small variations in the water or gas mixing rates can cause the loss of foam stability. Pumping pressures will be large compared with gelled water. It is also very difficult to get high sand concentrations in foam fracturing (Ely, 1998).

## 2.11 Additive Of Fracturing Fluids

The common fracturing additives described by Ely and et al, encompass their cons and pons: are breakers, biocides, fluid-loss additives, friction reducers and acid corrosion inhibitors. Simply put, biocides are added to kill bacteria that produce enzymes that break down gelling agents in fracturing fluids and reduce their effectiveness. Generally biocides, bactericides and microbicides are added to the mixing tanks to kill microorganism, but these can be inherently dangerous if not handled carefully. Fluid-loss additives help keep the fluids “together” and restrict leak-off of the fluid into exposed rock at the fracture face (Ely, 1998).

**Table 2.5 Fracturing Fluids Additives (Ely, 1998).**

<b>Fracturing fluid or additive</b>	<b>Positive</b>	<b>Negative</b>
Gelled fluids	Increased propanant carrying capacity. Work well with low temperatures. Low cross-link gels	Increased cost
Foamed gels	Good for low pressure formations can be combine with gelled fluids to increase effectiveness	Reduced propanant carrying expensive equipment
Acids	Can be used to clean the wells	Required large amounts
Breakers	Enhanced post-fracturing fluids recovery	Some fluids required large amounts
Biocides	Kills bacteria and microorganism	Can be dangerous to the environment
Fluids-loss additives	Reduced "leakoff"	Increased cost
Frictions reducers	Reduced friction in well and pumps	Increased cost
Acid crossition inhibitors	Prevent corrosion of the equipment	Increased cost



## **2.12 Water for Hydraulic Fracturing**

Several studies have assessed water resource demands in world. All of these studies base the total water demands on the number of wells. Typically the water required to drill and hydraulically fracture a well is estimated to be between one and five million gallons per well (Goodwin et, al. 2013).The study found that the total water use for vertical wells remains relatively constant. However, the total water use for horizontal wells can vary from a few hundred thousand gallons up to nearly eight million gallons per well. These general estimates of water use have led to increased uncertainty and conflict surrounding water development for the oil and gas industry in the world. The amount of water used to hydraulic fracturing processes includes several categories such as: (Katie Guerraet, al 2011).

1. Hydraulic fracturing water consumed;
2. Total water consumed;
3. Well type (vertical, horizontal, or extended horizontal);
4. Hydraulic fracturing stages or distance;
5. Hydraulic fracturing fluid;
6. Well coordinates;
7. Target formation, if available.

What does the reservoir rock need, and what will the rocks give back after fracturing? Important questions to manage the water for hydraulic fracturing; the choice of the fracturing fluids dictates the frac design and what types of fracturing fluids and additives are required. The choice of the frac fluids dictates the fate and transport of fracturing fluids used in fracturing operations, and how the recovered will need to be managed and disposed (American Petroleum Institute, 2010). The water for hydraulic fracturing may be obtained from different sources:

1. Surface water,
2. Groundwater,
3. Municipal water supplier,
4. Treated wastewater for Municipal and industrial treatment facilities,
5. Power plant cooling water,
6. Recycle produced water or/and flow back water.

The best selection will depend upon volume and water quality requirements, regulatory and physical availability, competing uses, and characteristics of the formation to be fractured (including water quality and compatibility consideration). Fresh water specification is the best option; however, the operations should consider using non-potable (may saline and contain high total dissolved solids) water for drilling and hydraulic fracturing may be because of uncertain and limitation of fresh water.

### **2.13 Produced Water For Hydraulic Fracturing**

The use of produced water for hydraulic fracturing has many advantages, such as (Bankole & Blauch, 2014).

1. Mitigating in disposal of produced water.
2. Reduction of fresh water consumption during completion and production operation.
3. Realization of economic benefits the operator.

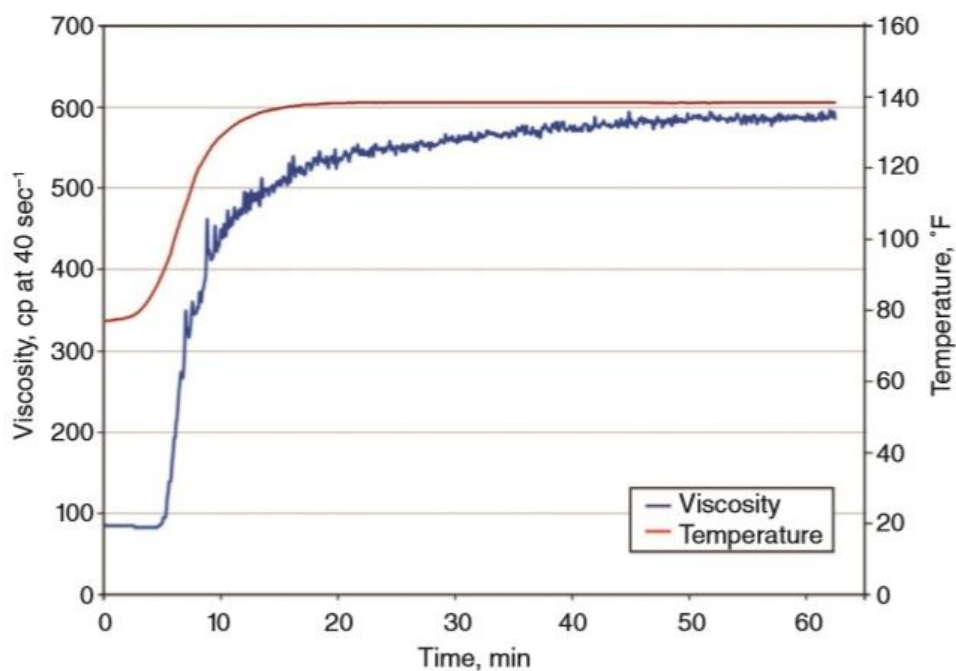
In some basins, the use of produced water in oil and gas drilling and slickwater-based fracturing treatments has been explored. Typically, these applications use water with low TDS levels. Little work has been done on the use of produced water with high TDS levels (>200,000 ppm) in fracturing fluids designed with linear or crosslinked gel bases(Lord et, al. 2014).

The salinity, total dissolved solids (TDS) and overall quality of this water/flow back mixture can vary by geologic basin and specific rock strata. For instance, water salinity can be range from brackish (5,000 part per million (ppm) to 35,000 ppm TDS), to saline from (35,000 ppm to 50,000 ppm TDS), to supersaturated brine from (50,000 ppm to > 200,000 ppm TDS) American Petroleum Institute, 2010).

Some studies were conducted to examine the applicability of using seawater instead of fresh water specially in offshore drilling because of the location limitation, Poor viscosity was observed possibly due to the reduction of the effective crosslinker concentration resulting from pH shift and chelation. Proper rheological characteristic of the fracturing fluid is crucial to the success of the stimulation treatment. Loss of fluid viscosity can lead to ineffective proppant transport, distribution, and placement as well as reduced fracture geometry resulting in loss of revenue (Huang et, al. 2005).

## 2.14 Preparation of Hydraulic Fracturing Fluids

To fracture the formation, special fracturing fluids are injected down the well bore and into the formation under high pressure. The concentrations of these are different according to the several factors. Sometimes may include be fluids typically consist of approximately 90% water, 9.5% sand, and 0.5% chemicals. Sometimes water consume by hydraulic fracturing contains more than 99% of water and sand, the percentage of - additives in typical hydraulic fracturing fluids is usually less than 0.5% by total volume, the quantity used in these hydro-fracturing is so large that the additives in more than million gallon hydro-fracturing operation will be considerable. The volume of fluids used for this purpose depends upon a variety of factors, including the well type and the formation depth and geologic composition. For example, horizontal wells require more water than vertical or directional wells (because of the length of the borehole that will be fracture stimulated), and deeper shale formations require more water than shallower coal bed methane formations.



**Fig 2.3 Fluid Rheology-Treated Produced Water. (Lord Et, Al. 2014).**

In 2011 J. Daniel Arthur summarize reduce of produced water in different applications and described the cons and pros of their application in a blow tables.

**Table 2.6 Water Minimization Technologies**

<b>Approach</b>	<b>Technology</b>	<b>Pros</b>	<b>Cons</b>
<b>Produced water</b>			
Reduce the volume of water entering the wells	Mechanical blocking devices (e.g., packers, plugs, cement jobs)	These should be used in new construction. They can be added later on to fix some problems	May not be easy to fix pre-existing problems
	Water shut-off chemicals (e.g., polymer gels)	Can be very effective in Selected instances.	Need the right type of formation in order to achieve cost-effective results.
Reduce the volume of water managed at the surface by remote separation	Dual completion wells (downhole water sink)	Can be very effective in selected instances	Limited prior use. Makes wells more complex
	Sea floor separation modules	May be a good future Technology	Cost is very high. Only two of these have ever been installed through 2009
Reduce the volume of water managed at the surface by remote separation	Dual completion wells (downhole water sink)	Can be very effective in selected instances	Limited prior use. Makes wells more complex
	Sea floor separation modules	May be a good future Technology	Cost is very high. Only two of these have ever been installed through 2009

**Table 2.7 Water Re-Use and Recycle Management Options**

Management Option	Specific Use	Pros	Cons
<b>Produced water</b>			
Re-injection for enhanced recovery	Water flood; steam flood; SAGD (steam assisted gravity drainage) for oil sands	Common use of produced Water for onshore wells. Usually has low cost.	Need to ensure chemical compatibility with receiving formation
Injection for future water use	Aquifer storage and Recovery	Great option when possible. Only one actual example (Wellington, Colorado).	Need to ensure that water meets drinking water standards before injecting it into a shallow aquifer. May encounter public opposition
Injection for hydrological purposes	Subsidence control	Can help solve a local problem (e.g., Long Beach, CA).	Need to ensure chemical compatibility with receiving formation
Agricultural use	Irrigation; subsurface drip irrigation	Can provide a source of Water for animals.	May need to treat the water before applying it to the soil or add soil supplements
	Livestock and wildlife Watering	Can provide a source of water for animals	Need to ensure that water is clean enough to avoid illness or other impacts to animals
Use flowback water for future frac fluids	Use after settling, filtration, or other basic treatment step	Several Marcellus Shale operators began doing this in2009-2010. Saves disposal fees, transportation costs, and requires less new water for next frac job.	Must have a new well waiting to be fracked so long-term water storage is avoided. Limited data are available about lifetime productivity of wells fracked with these fluids, but initial results look excellent

**Table 2.8 Water Disposal Technologies**

<b>Technology</b>	<b>Pros</b>	<b>Cons</b>
Discharge	Very common for offshore facilities. Offers moderate cost and acceptable environmental impact, where permitted	Not approved for most onshore wells. Where allowed, requires treatment unless the water is high quality, such as some CBM effluent.  Different treatment requirements for discharges into different types of water bodies
Underground injection (other than for enhanced recovery)	Very common onshore practice. Tends to have low cost. EPA and state agencies recognize this as a safe, widely used, proven, and effective method for disposing of produced water	Requires presence of an underground formation with suitable porosity, permeability, and storage capacity. May require treatment To ensure that injectate does not plug formation. UIC permitting in two key Marcellus Shale states that do not have delegated authority to administer the UIC program (PA and NY) can be very time consuming. For these states, the EPA Region III office issues UIC permits.
Evaporation	In arid climates, takes advantage of natural conditions of humidity, sun, and wind	Not practicable in humid climates. May create air quality and salt deposition problems
Offsite Commercial disposal	Provides service to oil and gas community by accepting and disposing water for a fee.  Removes water management burden from the operator	Requires infrastructure (disposal facilities and transportation network to move water to disposal site). Can be costly. Potential for Superfund liability

## 2.15 Produced Water Treatment

Produced water always contains high concentrations of TDS, TSS, metal ions as well as oil and grease. To ensure the injected produced water is confined in the injection zone in a manner that does not contaminate the water bearing geologic formation, produced water needs to be treated before injection. Therefore, to meet the EPA and API and RCRA regulations, removal of TDS, TSS, oil/grease, and metal ions are the main treatment goals.

Physical, chemical and biological methods are used to remove contaminants from waste-water. In order to achieve different levels of contaminant removal, individual waste-water

treatment procedures are combined into a variety of systems, classified as primary, secondary, and tertiary waste-water treatment.

### **2.15.1 Free Water Knockout Vessel**

The first step of production stream goes to a separation unit called the Free Water Knockout Vessel (FWKV). In this unit free water and loose solids are separated from oil. And then Produced water from this unit is stored in Water Tanks, while the remaining oil and oil-water emulsion are additionally treated. In Treater Vessels with the combination of heat and some chemicals (Emulsion Breakers or Demulsifiers) oil-water emulsions are broken down and clean oil, water and some solids are produced. Clean oil goes to storage or shipping and produced water is kept for disposal in Water Tanks. Depending on the residence time some of the solids may settle out of the water and residual oil in the water floats to the surface. This oil layer is skimmed off the top and recycled to recover this additional oil.

### **2.15.2 Skim Tanks and Vessels**

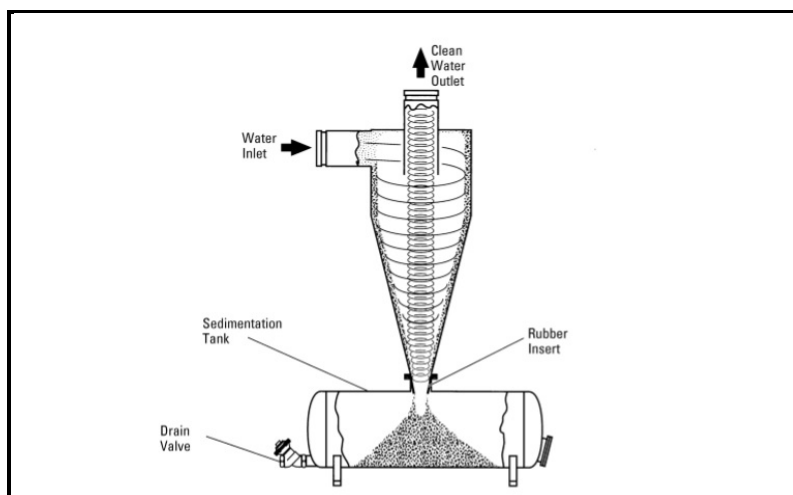
Skim tanks and vessels are very simple equipment for treating the waste water (primary treatment). They have the same shape, components and functionality. The main difference between them is that the skim tank is operated under the atmospheric pressure. For providing the sufficient time (10-30 minutes) for coalescing and separating of oil droplets their volume is very large (Clauss & Kuhnlein, 1992).

### **2.15.3 Separation Techniques Based on Filtration (Filters)**

A well-known technique for separating non soluble components is by filtration. Several principles for handling produced water have been considered including microfiltration membranes and media filters. Such treatment technologies are potentially advantageous because of very good separation degrees can be achieved. However microfiltration has found very limited practical application because of cost and poor operability, very high energy consumption and degradation of the filters elements with use (Gregoire, 2008).

### 2.15.4 Cyclonic Separation Methods

The advanced methods that most commonly used technology in offshore production since around 1990 is the static hydro cyclone that utilizes available pressure for enhanced speed in gravity separation. The advantages for this equipment type are high reliability (no moving parts), low maintenance, requires very little space, and gives good separation effect and high capacity. Hydrocyclones can remove particles in the range of 5–15 mm and have been widely used for the treatment of produced water this description given by (Igunnu & Chen, 2012).



**Fig 2.4 Hydro cyclone Flow and Mode of Separation (Igunnu & Chen, 2012)**

### 2.15.5 Precipitations (Precipitators)

The technologies of precipitators the water is forced to flow through a porous media present in a vessel arranged horizontally that resemble the three phase separator so enhance the coalescing of oil droplets. Then this result in oil droplets with greater size and increase the rate of its flow in the upward direction encounter to the down movement of water then this oil can be removed out from the vessel. This method is very effective in the treatment of the waste streams and attaining the desired quality. The problem of plugging the porous material limits the use of this type(Eisenman 2005).



### **2.15.6 Membrane Filtration Technology**

Membrane filtration technology could be considered microporous films with specific pore ratings, which selectively separate a fluid from its components and Classified into four types. Each type it has limit pore size and specific condition for removing certain impurities (Igunnu & Chen, 2012).

- Microfiltration/ultrafiltration
- Ultrafiltration
- reverse osmosis
- nanofiltration

### **2.15.7 Thermal Technologies**

Thermal treatment technologies of water are employed in regions where the cost of energy is relatively cheap U.S. Bureau of Reclamation and Hamed; gave the idea of range and classification of thermal technologies. Thermal separation process was the technology of choice for water desalination before the development of membrane technology. The major thermal desalination technologies are:

- Multistage flash (MSF) distillation,
- vapour compression distillation (VCD) and
- multieffect distillation (MED)

### **2.15.8 Gas Flotation**

The technology is widely used for the treatment of conventional oilfield produced water (C, akmaç, et al 2008). This process uses fine gas bubbles to separate suspended particles that are not easily separated by sedimentation. When gas is injected into produced water, suspended particulates and oil droplets are attached to the air bubbles as it rises. This results into the formation of foam on the surface of the water which is skimmed off as froth. There are two types of gas flotation technology (dissolved gas flotation and induced gas flotation) based on the method of gas bubble generation and resultant bubble sizes. In dissolved gas flotation units, gas is introduced into the flotation.

### **2.15.9 Electrocoagulation Methods**

One of the best new technologies for treating produced water called electrocoagulation (EC), conducted in the Permian Basin to prepare cross-linked fluid. In EC, an electric current is applied across metal plates to remove various contaminants from the water. Heavy metals (ions) and colloids (organics and inorganics) are primarily held in solution by electrical charges and particle size. The electrical charge applied to the solution of contaminated water destabilizes the charges on the particles and generates a coagulation reaction. (Lord et, al. 2014).

### **2.15.10 Electrochemical Techniques**

It suggests that treatment technologies based on electrochemistry could be the future of produced water management, since produced water is a potential electrolyte because it has a relatively good conductivity. It also explains that by applying photo electrochemistry, water electrolysis, fuel cell and electrode position, electrochemical engineering could achieve energy storage, production of clean water and recovery of valuable metals from produced water with minimal or no negative impact on the environment(Igunnu & Chen, 2012).

### **2.15.11 Ion exchange technology**

Ion exchange process effectively removes arsenic, heavy metals, nitrates, radium, salts, uranium, and other elements from the produced water (Clifford DA, 1999). Ion exchange is a reversible chemical reaction wherein positively or negatively charged ions present in the water are replaced by similarly charged ions present within the resin. The resins immersed in the water are either naturally occurring inorganic zeolites or synthetically produced organic resins. When the replacement ions on the resin are exhausted, the resin is recharged with more replacement ions.

Nadav, suggested that ion exchange has the potential to remove boron from RO permeate of produced water. Ion exchange technology has a lifespan of approximately 8 years and will require pre-treatment options for solid removal. It also requires the use of chemicals for resin regeneration and disinfection. The operating cost accounts for more than 70% of the overall cost of this technology (Nadav, 1999).

There are a lot of conventional and advanced technologies for produced or waste water treatment processes such as without details:

- Chemical oxidation
- Media filtration
- Freeze thaw evaporation
- Electro dialysis/electro dialysis reversal
- Adsorption
- Evaporation pond
- Macro-porous polymer extraction technology
- Biological aerated filters

### **2.15. 11.1 Treatments by Zeolites (Ion Exchange)**

Several studies have been confirmed that the removal of metals by zeolite from waste water treatment becomes very suitable choice and more feasible, because of low cost and very little attention. They are two types of zeolite, natural and synthetic. Almost forty-one naturally occurring zeolites have been found and several others have been synthesized, of which the most popular natural zeolite is clinoptilolite. The synthetic zeolites have replaced the natural ones because of their higher thermal stability and selectivity in catalytic reactions (Wang et al. 2007).

**Natural Zeolites:** Most of the natural zeolites are safe, environmentally friendly, naturally occurring materials that are aluminosilicate and have an open box-work crystal structure which is occupied by cations and water molecules. These ions and water molecules can move within the large cavities allowing ionic exchange and reversible rehydration. The structures of zeolites consist of three-dimensional framework of  $\text{SiO}_4$  and  $\text{AlO}_4$  tetrahedra (Shaheen et al. 2012). The aluminium ion (Al) is small enough to occupy the position in the center of the tetrahedron of four oxygen atoms; the isomorphous replacement of  $\text{Si}^{4+}$  by  $\text{Al}^{3+}$  produces a negative charge in the lattice. The net negative charge is balanced by the exchangeable cation [sodium (Na), potassium (K) or calcium (Ca)]. These cations are exchangeable with certain cations in the solution such as Pb, Cd, and Mn (Ibrahim et al. 2010).

Most common of natural zeolites are formed by alteration of glass-rich volcanic rocks (ruff) with fresh water in the playa lakes or by sea water (Mohamed et, al. 2009). Natural zeolites have low organic carbon contents (<0.5%) and do not favour sorption of organic compounds. However, natural zeolites have been found to effectively remove several types of metals, such as lead and strontium, from aqueous solutions (Erdem et, al. 2004).

Natural zeolites are hydrated aluminosilicate minerals with cage-like structures. They have very high internal and external surfaces areas and high internal and external cation exchange capacities (CEC)(Haggerty & Bowman, 1994).

Moreover, natural zeolites are classified as low cost adsorbents because of their local availability and low cost extraction and preparation. Natural zeolite also gained a significant interest among scientist, because of their valuable properties such as ion exchange ability and high surface area.

**Synthetic Zeolites:** A huge types of synthetic zeolite used in industrial processes, preparation of synthetic zeolite by kaolin is most common methods. The important one was prepare by Egyptian kaolin and Commercial sodium silicate solution ( $\text{Na}_2 \text{Si}_2 \text{O}_5$ ) was used as source for silicone which analysed via X-ray fluorescence and commercial sodium hydroxide was used as alkaline solution with different concentration percent according to the type of prepared zeolites(Ibrahim et, al. 2010).

Other type of synthetic zeolite prepared from fumed silica as silica source and sodium aluminate as aluminium source they produced type of zeolite called A, efficiently accurately enhanced removal heavy metals according to changing of several factors (Ismail et, al. 2010).

Other zeolite from a source of Kaolin material called 4A, was prepare In Brazil work conducted for removing metals ( $\text{Na}^+, \text{K}^+, \text{Mg}^{2+}, \text{Ca}^{2+}, \text{Sr}^{2+}$ ) from waste water from Kaolin

material was used as Si and Al source. Controlled conditions and  $\text{SiO}_2/\text{Al}_2\text{O}_3$ ,  $\text{Na}_2\text{O}/\text{SiO}_2$  and  $\text{H}_2\text{O}/\text{Na}_2\text{O}$  appropriate stoichiometric ratios were used (Abreu et al. 2012).

There are many type of zeolites were prepared from kaolin, 3A zeolite was prepare from Venezuelan kaolin under certain conditions Kaolin ( $\text{Al}_2\text{O}_3 \times 2\text{SiO}_2 \times 2\text{H}_2\text{O}$ ) was subjected to to produce ( $\text{Al}_2\text{Si}_2\text{O}_7$ ) and then was zeolitized, producing 4A zeolite. The process involved the calcination of the kaolin at ( $750.0^\circ\text{C} \pm 0.1^\circ\text{C}$ ) for 5 h, in a muffle furnace Heraeus Electronic (Dreieich, Germany), suitable for removing  $\text{Pb}_2^+$  from wastewater (Rondón et al. 2013). For sorption performance scan electron microscopy (SEM) was used for zeolite characterization (Zhang et al. 2014). Other type called 4A was prepared from sol-gel process in presence of different silica and aluminium source. Main source of silica was-silica fumed, Si/AL mole ratio=2,  $\text{H}_2\text{O}/\text{SiO}_2$  mole ratio=150,  $\text{Na}_2\text{O}/\text{SiO}_2$  mole ratio=1.15, crystallization temperature  $110^\circ\text{C}$  and crystallization time 4 days the source of silica and aluminium were mixed together under certain condition and then produced that type of zeolite (4A) for removing metals ( $\text{Cu}^{2+}$ ,  $\text{Cr}^{3+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Ni}^{2+}$ ) (Mohamed et al. 2009). a below fig shows the effect of pH value on heavy metals ions uptake, % under the conditions reaction: zeolite dose 1g, volume of heavy metals solution; 100ml; initial ions concentration, 10 ppm for shaking time 60min at reaction temperature  $30^\circ\text{C}$ .

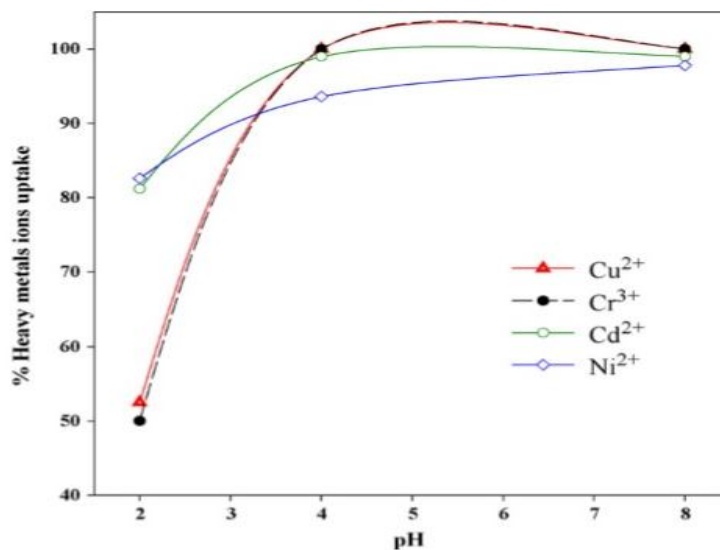


Fig 2.5 Effect Of Ph Value On Heavy Metals Adsorption (Mohamed et al. 2009)

**Table 2.9 Chemical and Physical Composition of Natural Egyptian Kaolin (Wt. %) (Ibrahim et, al. 2010).**

Chemical Composition %		Physical Composition	
SiO <sub>2</sub>	52.7	pH	7.5
Al <sub>2</sub> O <sub>3</sub>	31.4	Appearance porosity	41
TiO <sub>2</sub>	2.2	Appearance density (g/cm <sup>3</sup> )	2.20
Fe <sub>2</sub> O <sub>3</sub>	1.1	WEIGHT of per unit volume	1.30
MnO	0.01	Water absorption( original)	30.3
MgO	0.21	Water absorption(grinding)	102.6
CaO	0.52	Original bleaching	1.94
Na <sub>2</sub> O	0.1	Active bleaching	1.90
K <sub>2</sub> O	0.04	Ignition loss	0.14

### 2.15.11.2 Adsorption and Ion Exchange Processes In Produced Water By Zeolite

Zeolites are the best alternative methods for removing metals heavy metals from produced water they are widely studied as low-cost ion exchangers for the treatment of produced water containing inorganic solutes.

The process of adsorption capacity by zeolite depends on several factors such as initial concentration of metal ions and zeolite, temperature, particle size of zeolite, contact time and pH. It is well known that increasing pH, metal complexes can be formed due to reactions with the inorganic ligands present in produced water, such as CO<sub>3</sub><sup>2-</sup>, SO<sub>4</sub><sup>2-</sup>, OH<sup>-</sup>, PO<sub>4</sub><sup>3-</sup> and CH<sub>3</sub>COO<sup>-</sup> which are more or less soluble and can influence in the process of ion exchange (Abreu et, al. 2012).

The best adsorption capacity of the Fluoride adsorption with the natural zeolite modified zeolite was found to be better at acidic pH comparable to the factors from the solution chemistry that affected fluoride removal from water and waste water (Rahman et, al. 2010). A below table shows the comparison results of metals ions by different methods include zeolite.

**Table 2.10 Metal Ions Removal From Produced Water By Various Methods (Abreu et, al. 2012).**

Ions	Material	Removal (%)
Ca <sup>2+</sup> , Mg <sup>2+</sup> , Na <sup>+</sup> , K <sup>+</sup> , Sr <sup>2+</sup>	Zeolite 4A	60 – 99
Zn <sup>2+</sup> , Cd <sup>2+</sup> , Cr <sup>3+</sup> , Pb <sup>2+</sup>	Sponges-like Luffa cylindrica	66 – 92
Ca <sup>2+</sup> , Mg <sup>2+</sup> , K <sup>+</sup> , N <sup>+</sup>	Electrodialysis	50
Na <sup>+</sup> , K <sup>+</sup> , Ca <sup>2+</sup> , Mg <sup>2+</sup>	Carbon aerogel-based	8-22
Ni <sup>2+</sup> , Cd <sup>2+</sup> , Cr <sup>3+</sup>	Waste stabilization ponds	95-99

Ismail et, al. shows in following tables the effect of diffent parmeters such as zeolite dose, concentration of heavy metals, reaction time and pH in adsorption capacity(Ismail et, al. 2010).

**Table 2.11: The Effect of Zeolite Dose on Adsorption Capacity**

Zeolite dose (g)	Heavy metal (%)			
	Cu	Cr	Cd	Ni
0.05	42.85	17.64	16.66	6.47
0.1	86.95	94.97	50.0	35.97
0.2	90.47	88.23	66.67	35.28
0.5	100	98.7	69.4	36.5

**Table 2.12: The Effect of Metal Concentration on Adsorption Capacity**

concentration of heavy metals mixture (ppm)	Heavy metals ions uptake (%)			
	Cu	Cr	Cd	Ni
50	100	97.05	69.4	35.28
100	100	98.7	68.1	35.28
150	100	99.9	70.1	36.2
200	99.89	100	72.3	36.2
300	99.8	98.96	73.14	36.3
500	68.19	53.7	28.95	22.13
700	44.98	37.87	8.26	10.57
900	23.83	35.57	6.01	10.57
1000	20.47	32.86	3.32	3.76

**Table 2.13: The Effect of Temperature on Adsorption Capacity**

Reaction temperature °C	Heavy metals ions uptake (%)			
	Cu	Cr	Cd	Ni
30	97.08	98.54	71.42	35.48
40	94.75	96.17	64.38	33.23
50	96.5	95.62	68.18	34.62
70	99.87	99.54	7.26	40.52
90	99.87	100	76.2	37.28

**Table 2.14 The Effect of pH On Adsorption Capacity**

Effect of pH at small Concentration	Heavy metals ions uptake (%)			
	Cu	Cr	Cd	Ni
2	52.94	50	80.96	82.59
6	100	100	98.74	93.61
8	100	100	99.28	97.67

### 2.15.12 Water quality issues

The important part that may be effluence water management options for fracturing operations include concentration of hydrocarbons analysed as (oil and grease), total suspended solids (TSS), soluble organics, iron, calcium, magnesium, potassium and trace constituents such as benzene, boron, silicates and other constituents American Petroleum Institute, 2010). Whatever, if the produced water reused for purpose of injection for water flooding, hydraulic fracturing technique or dispose of, the most common factors affect and cause several problems (damage to the wells or corrosion into pipes or scale along producing systems) should be addressed inhibits such as:

- Ionic composition
- Chemical contaminants
- Suspended solids (TSS)
- Total dissolved solids (TDS)



- Scale and precipitate potential
- Oil/grease/hydrocarbon content
- Non-condensable gas content

All of the constituents in produced water represent potential injection water quality issues may affect in injection processes and stimulation techniques, however, most common factors should be address and reduced such as: TDS (total dissolved solids), oil and grease, metal and heavy metals and bacteria.

#### **2.15.12.1 Ionic Composition (Metals)**

Metals and other well-known heavy Metals and present in produced water in the form of dissolved ions or particle. Some studies have found that produced waters tend to contain zinc (Zn), lead (Pb), manganese (Mn), iron (Fe), Aluminium (Al), Cobalt (Co), Phosphorus and barium (Ba) at concentrations widely exceeding the norms specified in regulations. For instance, Heglig oil field has low concentration of heavy metals which of them inhibits by bioremediation processes treatment that was done in site of the field.

Most oilfield formations contain a variety of fine-grained materials that may be susceptible to either movement (migration) or structural alteration (swelling or dispersion) due to contact with non-equilibrium injection fluids. A family of these materials, that can be especially reactive due to their cationic affinity, are commonly referred to as 'clays' and consist of a wide range of alumino-silicate based compounds. Common oilfield clays include smectite, mixed layer clay, illite, chlorite and kaolinite.(Bazin et, al. 1994) (Scheuerman & Bergersen, 1990).

Most oilfield clays are stabilized in place by the attraction of positively charged cations, such as Na<sup>+</sup>, K<sup>+</sup>, H<sup>+</sup>, Ca<sup>++</sup>, Mg<sup>++</sup>, etc., which are dissolved in solution in the brine that is contacting the clay surface.smectite or mixed layer (smectite/illite) clay, which is one type of reactive clay commonly present in many sandstone formations targeted for injection, most notably in shallower, low temperature, more immature sediments. Clay swelling lead to several problems and that may be reduced or mitigated by the flowing:

1. Increasing the total concentration of mono and/or divalent cations in the injection water by chemical additions or blending with more appropriate saline makeup water sources.(Bazin et, al. 1994)(Scheuerman & Bergersen, 1990).
2. Additional stabilizing chemical agents such as high valency amines, cationic polymers, etc., to stabilize clays on a temporary or permanent basis in the near wellbore area.
3. Use of high concentrations of caustics (KOH) to pre-treat the near injection well to stabilize clays(Sloat & Larsen, 1984)(Sloat, 1990).
4. Wettability altering agents to generate a strong oil-wet condition in the near wellbore region to increase water phase relative permeability and isolate reactive clays from direct water contact.

#### **2.15.12.2 Total dissolved solids (TDS)**

Total dissolved solids (TDS) or salts in form of Salinity are one of the most concerning aqueous constituents of either conventional or unconventional oil or gas produced water. Concentrations of TDS, ions, and even organic matter can vary by multiple orders of magnitude for different basins and fields. Dissolved solids may range from a few parts per thousand to the saturated level, and most produced water, especially shale gas produced water, has greater salinity than seawater, probably as a result of the water flowing through semipermeable shale units. Similar to seawater, produced water is usually dominated by sodium and chloride but at much greater levels than seawater, due to the evaporation of seawater in the formation reservoir(Anon n.d.). The most major ions present in produced water are calcium; magnesium, potassium and bicarbonate the concentration of sulfate and carbonate are low in most produced water, which allows the presence of a relatively high concentration of barium and strontium. Other ions such as phosphate, nitrite, ammonium and sulfide concentrations are usually low, but in some produced waters are at elevated concentrations (Wedepohl, 1970). A below Figure reflected relation between TDS and well production, showed increasing trends either with the increasing of well production time or the water production volume.

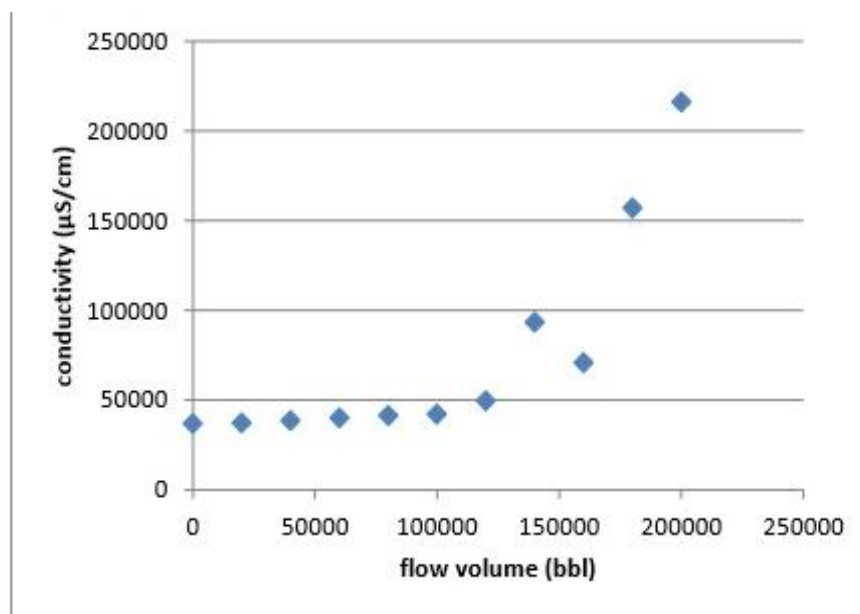


Fig 2.6 Conductivity change with produced flow volume (Timothy 2012)

### 2.15.12.3 Total Suspended Solids (TSS)

Solids analyses are important in the control of biological and physical wastewater treatment processes and for accessing compliance with regulatory agency wastewater effluent limitation. Concentration of solids may lead to plugging of the pore space in the near injection well region, due to the entrainment of suspended solids, can be rapid and severe, depending on the size distribution and concentration of solids which are in the injected fluid, volume of fluid injection and specific pore size distribution of the injection formation under consideration. Ideally, injection water should be pristinely clean and contain little or no suspended solids.

### 2.15.12.4 Oil and Grease

Oil and grease (OG) is an important parameter for water quality and safety. OG in water can cause surface films and films and shoreline deposits leading to environmental degradation, and can induce human health risks when discharged in surface or ground waters.

Additionally OG may interfere with aerobic and anaerobic biological process and lead to decreasing wastewater treatment efficiency.

How much oil can be safely tolerated in the injection fluids varies, depending on the oil and brine properties, the specific pore size distribution and wettability of the target formation. Based on general experience, oil and grease contents of less than 5 mg/l can be tolerated by most injection wells with in-situ permeabilities of greater than 20-30 mD (at lower permeabilities, sensitivity to oil content may increase). It might be better if the value oil and grease become zero to avoid any problems that associated with it.

#### **2.15.12.5 Bacteria**

Bacterial introduction into an injection well can occur during the drilling and completion/stimulation/workover, as well as during long term injection operations. Anaerobic bacteria notably sulfate reducing bacteria (SRB), generally tend to be the most problematic in oilfield situations, but, in some injection operations, if sufficient dissolved oxygen is present in the injection fluids, aerobic bacteria activity may also be an issue (Lappan & Fogler, 1992)(Horacek, 1992).

Most bacteria growth best at temperatures between 40-70°C, although some species of anaerobic bacteria can survive at temperatures in excess of 120°C. Even though reservoir temperature may be higher than the normal nominal range for bacterial growth, due to the large volumes of cool injection water that may be introduced into the near wellbore region and the relatively high heat capacity of water, a downhole cooling effect may occur even in high temperature formations and may lower temperature to conditions which may facilitate active biological growth.

Bacteria are problematic for a number response with respect to reducing injectivity, these being:

- Plugging of pore system due to bacteria (live and dead) as plugging solid particles.
- Plugging of pore system by polysaccharide polymer secretion from active colonies of growing bacteria in the formation.

- Plugging of the formation by corrosion products generated by bacterial growth on tubing, casing, surface equipment, etc. (as well as associated costs and equipment failures associated with corrosion issues).
- Generation of toxic H<sub>2</sub>S gas Generation of toxic H<sub>2</sub>S gas by metabolic action of SRB in-situ on elemental sulfate present in injection/formation waters (greater than 10 ppm of sulfate).
- Blockage / Plugging – hydrogen sulphide produced by SRB can react with solubilized iron formed as a result of corrosive and other processes in pipelines etc. to form insoluble, black ferrous sulphide. This in combination with organic or inorganic materials present in the water may clogs filters, valve and other equipment in water injection systems.

Plugging or corrosion (or both) the rocks by liberating H<sub>2</sub>S reducing permeability that is indicates to severe formation damage, so proper control of bacteria growth knowing which bacteria are responsible for plugging or corrosion, Since treatment is bacteria- specific. There are several ways to control bacteria heating or of bactericides.

Parameters should be conceders in water quality concern summarized in following Table.

**Table 2.15 Water Quality Test Parameters for Produced Water Reusing**

Inorganic components	Organic components	Others
Na, Ca, Mg	Total organic carbon	pH
Fe, Ba, B, Sr	Total carbon	Electric Conductivity (EC)
HCO <sub>3</sub> <sup>-</sup> /CO <sub>3</sub> <sup>-2</sup> , SO <sub>4</sub> <sup>-2</sup> , PO <sub>4</sub> <sup>-3</sup>	-	TDS, TSS

**Table 2.16 Water Quality Vs Fracturing Performance**

Concern	Water Parameter	Impact
Friction Reducer	Multivalent Ions	Can Impair Effectiveness and Drive Up Horsepower
Scaling	CaCO <sub>3</sub> CaSO <sub>4</sub> Ba <sub>4</sub> SrSO <sub>4</sub> FeSO <sub>4</sub>	Equipment and Line Fouling Loss of Formation
Bacteria	Sulfate Reducing Bacteria	Sour Formation (H <sub>2</sub> S)
Metals	Iron (Fe)	Formation Plugging (Iron Oxides)
Suspended Solids	Sand, Silts, Clays, Scale Particles	Formation Damage, Loss Permeability

### 2.15.13 Formation damage during injection and fracturing processes

Laboratory and field studies indicate that almost every operation in the field - drilling, completion, workover, production, and stimulation - is a potential source of damage to well productivity. The design of a team effort necessary for understanding and controlling of the formation damage problems in the field is necessary. The success of oil recovery is strongly influenced by whether the reservoir permeability can be kept intact or even improved. Permeability changes in petroleum reservoirs have received a great deal of concern by the oil and gas industry. The formation damage in scaled-up production wells caused by incompatibility of injected and formation waters have long been known. Permeability decline due to precipitate of salts. Among the most onerous of all scaling species is that of sulfates, particularly barium and strontium sulphites (Oddo and Tomson, 1994). If formation damage is suspected to be the cause of a well's low productivity, there are many techniques available to evaluate a well in order to identify this problem (Manual, 2006).

The chemical conditions of different types of brine cause the various precipitations. Table:(2.15) lists some common scale-forming compounds and reasons which cause these scales in the oil and gas plays (Moghadasi et al. 2003).

**Table 2.17 Common Oilfield Scale**

Name	Chemical Formula	Primary Variables
Calcium carbonate	CaCO <sub>3</sub>	Partial pressure of CO <sub>2</sub> , temperature, total dissolved solids, pH
Calcium Sulfide		Temperature, total dissolved solids, pressure
Gypsum	CaSO <sub>4</sub> ·2H <sub>2</sub> O	-
Hemihydrate	CaSO <sub>4</sub> ·0.5H <sub>2</sub> O	-
Anhydrite	CaSO <sub>4</sub>	-
Barium Sulfate	BaSO <sub>4</sub>	Temperature, pressure
Strontium Sulfate	SrSO <sub>4</sub>	Temperature, pressure, total dissolved salts
Iron Compounds	-	Corrosion, dissolved gases, pH
Ferrous Carbonate	FeCO <sub>3</sub>	-
Ferrous Sulfate	FeS	-
Ferrous Hydroxide	Fe(OH) <sub>2</sub>	-

The possible scaling occurring during oil and gas operations are carbonate scale and sulfate scale. Typical carbonate scale is carbonate calcium, and it is sometimes accompanied by iron carbonate. Carbon dioxide ( $\text{CO}_2$ ) can be found in three phase such as dissolved carbonate dioxide, carbonate ( $\text{CO}_3$ ) and bicarbonate ( $\text{HCO}_3$ ). Carbonate combined with calcium, iron or other metal ions will form scales(Kalantari-Dahaghi et al., 2006).

Usually carbonate scale is influenced largely by pH, temperature and pressure. For example, calcite scale formation ( $\text{CaCO}_3$ ) is usually a result of the pressure drop during gas and oil production. This pressure drop removes the carbon dioxide from the solution, the pH of the solution will increase and cause calcite precipitation. Also, a secondary consequence of the pressure drop is that the solubility of the calcite goes down with the decrease in pressure(Moghadasi et al., 2004).

During hydraulic fracturing process, high pressure is applied to create the fracture but this pressure increase will also drive the immigration of solids towards the wellbore causing some nearby areas to get clogged by those particles solids. In addition, temperature and pressure changes occurring during oil and gas production leads to a large gradient of pressure and temperature near the wellbore and surface, under which conditions precipitation will take place.

In order to prevent scaling and plugging due to reusing produced water for hydraulic fracturing, metal cations (scaling-form metals) should be measured before treatment, including calcium, magnesium, barium, iron and strontium. In addition, anions, such as sulfate and carbonate/bicarbonate, which would combine with these cations to create scale, also need to be analyzed. Integrated information about metal ions and scale anions will provide basic knowledge of the scale potential of certain produced water.

Boron is added as into the fracturing fluid as a cross-link chemical in the hydraulic fracturing process, so boron represents another parameter concern in produced water reuse. The concentration of boron present in the reclaimed water would affect the fracturing cross

linker's performance. Also several parameters should be consider, high total dissolved solids (TDS) increases friction in the hydraulic fracturing process, and high total solids can plug wells and decrease biocide effectiveness. Iron oxide will also cause plugging. The Manual on Formation Damage, (2006) described and expressed the damage during various phases of the oil and gas recovery and their Remedial Measures in the following Tables.

**Table 2.18 Formation Damage during Various Phases of Oil and Gas Recovery (Manual, 2006)**

<b>Operation</b>	<b>Formation damage</b>	<b>Remedial measure</b>
Drilling	Particle invasion/Filter cake	Matrix acidization, Perforation, Hydraulic fracturing
	Swelling and dispersion of indigenous Reservoir clays by the mud filtrate	Matrix acidization
	Mutual precipitation of soluble salts in the filtrate and formation water	Matrix acidization
	Water block/emulsion block	Surfactant treatment, matrix acidization
Cementing	Fine migration from the cement slurry into the formation	Matrix acidization, Perforation, Hydraulic fracturing
	Precipitation of solids from the cement within the formation	Matrix acidization, Perforation
	Precipitation of secondary minerals following reservoir mineral dissolution	Matrix acidization
Sand control	Fines migration	Acidization, Clay stabilization, Acidization with foam based fluids
	Perforation plugging	Acidization
Sand control	Fines migration	Acidization, Clay stabilization, Acidization with foam based fluids
	Perforation plugging	Acidization
	Polymer invasion	Surfactant treatment, Matrix acidization
Completion and workover	Hydration and swelling of clay minerals	Matrix acidization, Clay stabilization
	Movement and plugging by clay size particles in the formation	Matrix acidization, Clay stabilization
	Plugging by invading materials from the well bore fluids	Matrix acidization
	Emulsion and water blocks due to wellbore fluid loss	Surfactant treatment, Matrix acidization
	Relative permeability effects	Acidization
	Precipitation of scales	Acidization



	Plugged perforations due to improper perforating conditions	Acidization, perforation
Production	Fine migration	Deep penetrating acid treatment, Clay stabilization
	Scale deposition	Acidization
	Paraffin, wax & Asphaltene formation	Surfactant treatment, Solvent treatment
	Wettability alteration	Surfactant treatment, Solvent treatment
	Liquid block	Surfactant treatment
	Condensate banking	Hydraulic fracturing
	Emulsion generation	Solvent/Demulsifier treatment

**Table 2.19 Formation Damage during Stimulation and Injection Processes**

Operation	Damage mechanism	Remedial measure
Acidizing	Fines migration	Clay stabilization, Hydraulic fracturing
	Reaction and precipitation	Hydraulic fracturing, Acidization
	Sludge formation	Solvent treatment
	Emulsion formation	Surfactant treatment, solvent treatment
Hydraulic fracturing	Solid plugging	Refracturing with compatible fluids and proppants
	Emulsion blocks	Surfactant treatment
	Water blocks	Surfactant treatment
	Rock wettability change	Surfactant treatment
Water injection and different EOR methods	Solid invasion	Acidization, Hydraulic fracturing
	Fine migration	Acidization, Clay stabilization
	Clay swelling	High saline fluid
	Clay deflocculation	Surfactant treatment, Clay stabilization
	formation dissolution	Acidization, hydraulic fracturing
	Solid invasion	Acidization, Hydraulic fracturing
	Fine migration	Acidization, Clay stabilization treatment
	Clay swelling	High saline fluid
	Clay deflocculation	Surfactant treatment, Clay stabilization
	formation dissolution	Acidization, hydraulic fracturing
Skim oil entrainment	Surfactant treatment	

	Biologically induce impairment	Biocide treatment
	Sand influx	Sand consolidation treatment
	Chemical adsorption /wettability alterations	Surfactant treatment
	Formation of insoluble scales and emulsifications	Surfactant treatment, Solvent treatment
	Precipitate formation	Acidization